

# PYROLYSIS AND HYDROPYROLYSIS OF KENTUCKY OIL SHALE IN SUPERCRITICAL TOLUENE UNDER RAPID HEATING CONDITIONS

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## ABSTRACT

Oil shale from the Cleveland member of the Ohio shale, Montgomery County, Kentucky has been pyrolysed in supercritical toluene in the presence and absence of gas-phase molecular hydrogen. Data have been collected in a 300-cc stirred tank autoclave at residence times of 0<sup>+</sup>, 5, and 30 minutes, temperatures from 653 to 733 K, and total pressures (at temperature) ranging from 15.1 to 20.6 MPa. The reactor was equipped with a gas-driven sample injector so that shale could be injected into the pre-heated dense gas at reaction conditions. Heating rates of approximately 500 C/min were obtained with this configuration. Results for conversion of organic carbon to oil have been computed based on a carbon balance on the reaction system.

The objectives of the experimental program were:

- 1: investigate the use of toluene as a dense gas medium;
- 2: elucidate the reaction kinetics and the effect of hydrogen and heating rate on the rate and extent of oil formation. The data have shown toluene to be an excellent dense-gas media for facilitating supercritical pyrolysis and hydrolysis. Carbon conversions and oil yields of in excess of 185% of Fischer Assay were achieved in the presence of gas-phase molecular hydrogen at very short (<2 minute) residence times. Carbon conversion to oil was found to be a function of final temperature, hydrogen partial pressure, and heating rate.

## INTRODUCTION

Oil shale represents one of the largest hydrocarbon reserves in the world (1). Of the various techniques available for recovery of oil from oil shale, processes based on thermal decomposition of the organic matter in shale have received, by far, the most attention (2). Thermal decomposition or retorting technologies have been developed to a high degree of sophistication as evidenced by the TOSCO II, Union B, and Chevron. Unfortunately, retorting processes are plagued by inefficiencies in oil recovery which are inherent to the pyrolytic chemical reactions taking place. Principally, these inefficiencies result in low carbon conversion to oil due to free radical reactions such as cracking and condensation. In the case of cracking, a high gas make is promoted at the expense of oil while the oil product remaining is correspondingly high in olefin content. Regressive reactions due to condensation promote formation of coke. Both cracking and coking may be reduced to some extent by operation at low temperature and/or short residence times, or by processing in the presence of hydrogen and/or hydrogen transfer agents that act as free radical scavengers. It is the latter phenomenon that gives rise to interest in alternate oil shale processing schemes based on

reactions in dense gas media.

Kerogen in oil shale is known to be relatively insoluble in most organic solvents at or below their normal boiling points, but when oil shale is heated to temperatures above 600 K, the organic matter may be extracted in high yield (3,4). Several early patents describe solvent processing of torbanite and other shale-like materials at elevated temperatures both with and without hydrogen gas atmospheres (5,6,7,8). Jensen et al. (9) have reported on hydrogenation of Green River oil shale in vehicle oils, while Gregoli (10), Patzer (11), and Greene (12) have all recently been issued patents for hydrogenation of oil shale in hydrogen donor and non-donor solvents in the presence and absence of gas phase molecular hydrogen. Recently, McKay et al. (13) and Baldwin et al. (14) have reported on investigations using dense (supercritical) gases and subcritical fluids for extraction of shale oil from oil shale under a wide variety of processing conditions.

This paper presents the results of pyrolysis and hydrolysis of oil shale from the Cleveland Member of the Ohio shale group from Montgomery County, Kentucky. The objective of the research described was to investigate the effect of temperature, hydrogen partial pressure, time, and heating rate on carbon conversion and oil yield using toluene as the dense gas vehicle.

#### EXPERIMENTAL APPARATUS AND METHODS

All experiments were carried out in a 300-cc autoclave reactor, manufactured by Autoclave Engineers. The reactor was interfaced to an Apple II+ microcomputer for data acquisition and control of heating rate. A schematic of the system is shown in Figure 1. The as-received shale was processed by crushing (to 100% -200 mesh) and vacuum drying at 40 C. Dried shale was stored in a vacuum dessicator until used. A Fischer Assay of the feed shale is shown in Table 1. Also shown in this table are data on organic carbon conversion to oil for the Fischer Assay analysis, computed from quantitative analysis of the spent shale and retort gases for carbon, and a forced ash balance on the feed and spent shale. For the supercritical gas extraction experiments, helium and hydrogen were used as the reaction process gases, with a 1% krypton tracer employed so that gas make could be readily quantified. Spent shale recovered from the reactor was extracted with acetone and methylene chloride to remove adsorbed shale oil. Samples of the feed and spent shale were analyzed for total and inorganic carbon on a Coulometrics system.

#### DISCUSSION OF RESULTS

Experimental runs were made at temperatures between 653 and 733 K (380 and 460 C) in 20 degree increments, and at reaction times of 0, 5, and 30 minutes. Prior to initiating heating of the reactor, 2.06 MPa (300 psi) of either helium or hydrogen was added to the reactor. This initial pressure plus the autogeneous pressure of the solvent (toluene) resulted in a total pressure at reaction temperature of between 15.1 and 20.6 MPa (2200 to 3300 psi). At these conditions, toluene (critical temperature 593.9

K, critical pressure 4.07 MPa) was present in the reactor as a dense gas. After heating to reaction conditions with only gas and toluene present in the reactor, the shale was injected into the vessel with an overpressure of helium. The reaction temperature rapidly rebounded to the desired temperature (generally within one minute). Following the desired reaction time, the reactor was quenched by forced convection. Samples of the spent shale were analyzed for total and inorganic carbon, and ashed in a muffle furnace. Carbon conversion to oil plus gas was then calculated based on a forced ash balance, while carbon conversion to gas was calculated from an analysis of the reaction product gases. Carbon conversion to oil, and thus oil selectivity, was then finally computed by difference. In the following discussion, oil selectivity refers to the fraction of carbon converted that is converted to oil.

Two baseline runs in helium and hydrogen atmospheres were performed at 698 K in order to establish the thermal reactivity of the shale in supercritical toluene. These runs were, however, done with the reactor used in the true batch mode of operation where the entire reaction mass was heated slowly (approximately 8 C per minute) to the final temperature, and then held at this level for one hour. Results of this run are shown in Table 2. As may be seen, an organic carbon conversion of 44.0% and oil selectivity of 91.6%, resulting in an overall conversion of carbon to oil of only 40.3% was achieved in the absence of hydrogen. This conversion level is consistent with the results obtained in standard Fischer Assay pyrolysis (viz. Table 1). Pyrolysis under these conditions in the presence of hydrogen however raises the carbon conversion to oil to 68.9%, thus demonstrating the well-recognized benefits attendant to hydrolysis of aromatic oil shales. Clearly, hydrogen in the reaction gas atmosphere greatly enhances carbon conversion. This is primarily accomplished by inhibiting condensation reactions which lead to formation of coke, as the oil selectivities differ by only about 10%. This observation is consistent with a radical quenching mechanism, promoted by the presence of gas phase molecular hydrogen.

Results for pyrolysis and hydrolysis in supercritical toluene under rapid heating conditions (c.a. 500 C/min) are shown in Figures 2, and 3. Figure 2 presents the kinetic data for organic carbon conversion obtained with hydrolysis under rapid heating conditions at an initial (cold) hydrogen pressure of 300 psi. As may be seen, the low temperature isotherms (653, 673, and 693 K) exhibit the expected time/temperature behavior. Hydrolysis at 713 and 733 K however shows an entirely different behavior, with the organic carbon conversion reaction becoming essentially instantaneous at the highest temperature studied (733 K). Oil selectivity (the fraction of carbon reacted that is converted to oil) at the highest temperature and shortest residence time is 95.6%. This, coupled with the 61.3% organic carbon conversion achieved at this combination of reaction conditions gives rise to an overall oil yield in excess of 185% of Fischer Assay. Perhaps more interesting however, is the effect of hydrogen on the reaction that is indicated in Figure 3. As illustrated, under conditions of rapid heating and low final

temperature (673 K), the organic conversion is insensitive to the presence of hydrogen in the reaction gas atmosphere over a wide range of residence times as shown by the essentially identical results for pyrolysis (helium atmosphere) and hydropyrolysis. This is in direct contrast to the slow heating data shown in Table 2, where hydrogen has a marked effect on the ultimate yield of oil. At 713 K, the presence of hydrogen has a small beneficial effect at the short residence time (5 minutes), and a substantial beneficial effect at the extended residence time of 30 minutes. At 733 K, the effect of hydrogen is pronounced over the entire range of reaction times studied, and is especially pronounced at 30 minutes. Considering these data in light of the previous data from the slow heating rate experiments serves to indicate that a complex mechanism involving both radical quenching and oil evolution rate processes is operative in this reaction system. Under conditions of rapid heating but at low final temperatures (673 K or less) the secondary condensation reactions leading to decreased oil yield are apparently sufficiently slow such that the carbon conversion reactions are not sensitive to the presence of added hydrogen. Reaction at high heating rates but higher final temperatures (713 K and above) however shows a significant sensitivity to the presence of gas-phase molecular hydrogen, especially at extended residence times. Apparently, under these conditions, regressive (coke-forming) reactions are sufficiently rapid that inhibition of condensation by radical quenching becomes significant, thus leading to enhanced organic carbon conversions. At high heating rates, significantly higher organic carbon conversions can be obtained with inert atmosphere pyrolysis when compared to the Fischer Assay as shown by a comparison of the high temperature helium atmosphere data in Figure 3 and the data in Table 1. This enhanced yield is, however, only present at short residence times (<5 minutes). This is undoubtedly due to the well documented effect of "flash pyrolysis", where the rapid rate of volatiles evolution is successful in preventing secondary reactions which decrease carbon conversion (15). At higher reaction severity (time/temperature combinations), some form of hydrogen activity is required to prevent the onset of regressive reactions with the resultant loss of carbon conversion.

#### ACKNOWLEDGEMENTS

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FIGURE 1

Batch Reactor Schematic

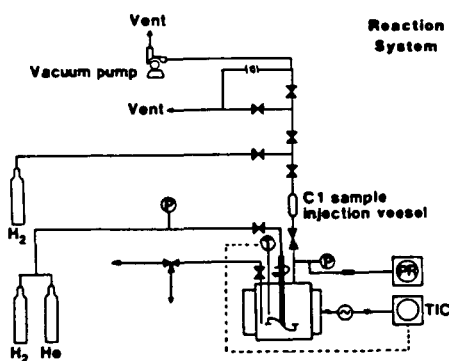


FIGURE 2  
Organic Carbon Conversion Isotherms

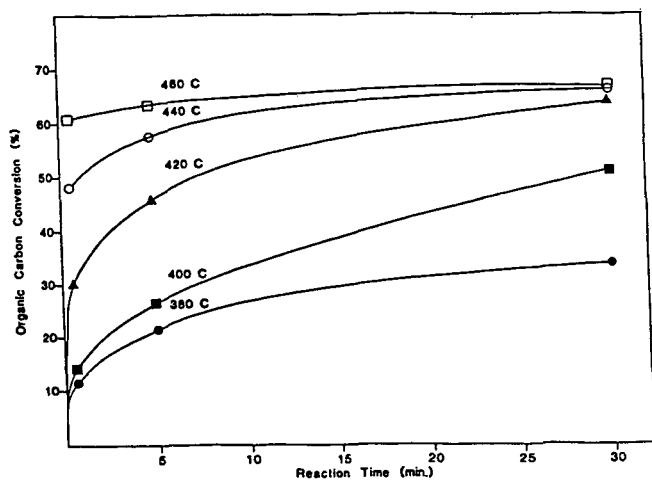


FIGURE 3  
Inert Gas and Hydrogen Atmosphere Comparisons

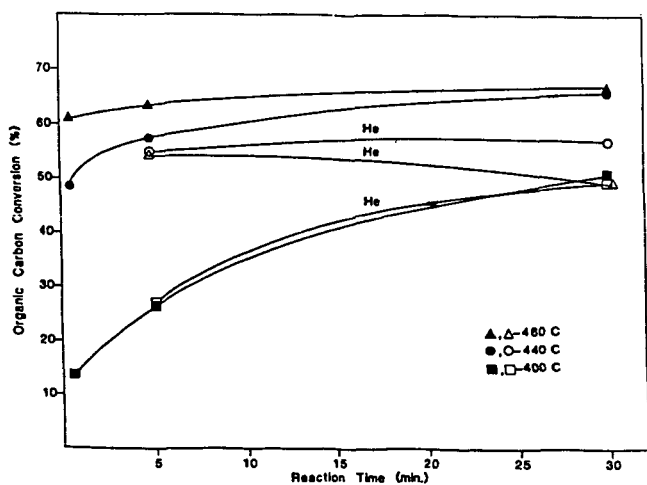


TABLE 1  
Analysis of Feed Shale

%spent shale	Fischer Assay <sup>1</sup>			oil, GPT	OCC <sup>2</sup>
	%oil	%water	%gas+loss		
91.6	4.6	1.5	2.3	11.6	42.9

1. Analysis by Commercial Testing and Engineering Co., Golden, CO
2. % organic carbon conversion to oil

TABLE 2  
Results under Slow Heating Rate Conditions<sup>1</sup>

	H <sub>2</sub>	He
OCC <sup>2</sup>	72.6	44.0
OY <sup>3</sup>	95.9	91.6

1. Reactions carried out in true batch mode, heating rate of approximately 8 C/min, 425 C final temperature, 300 psi initial hydrogen charge, 60 minutes residence time.

2. Organic carbon conversion to oil+gas, wt%.

3. Percent of organic carbon converted that is converted to oil.